

DISTINCT CHLORINE ISOTOPIC RESERVOIRS ON MARS. IMPLICATIONS FOR CHARACTER, EXTENT AND RELATIVE TIMING OF CRUSTAL INTERACTION WITH MANTLE-DERIVED MAGMAS, EVOLUTION OF THE MARTIAN ATMOSPHERE, AND THE BUILDING BLOCKS OF AN EARLY MARS. C.K. Shearer^{1,2}, S. Messenger³, Z.D. Sharp², P.V. Burger¹, N. Nguyen^{3,4}, and F.M. McCubbin³.

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Introduction: The style, magnitude, timing, and mixing components involved in the interaction between mantle derived martian magmas and martian crust have long been a point of debate [1-6]. Understanding this process is fundamental to deciphering the composition of the martian crust and its interaction with the atmosphere, the compositional diversity and oxygen fugacity variations in the martian mantle, the bulk composition of Mars and the materials from which it accreted, and the noble gas composition of Mars and the Sun. Recent studies of the chlorine isotopic composition of martian meteorites imply that although the variation in $\delta^{37}\text{Cl}$ is limited (total range of $\sim 14\%$), there appears to be distinct signatures for the martian crust and mantle [7,8]. However, there are potential issues with this interpretation. New Cl isotope data from the SAM instrument on the Mars Science Lab indicate a very wide range of Cl isotopic compositions on the martian surface [9]. Recent measurements by [10] duplicated the results of [7,8], but placed them within the context of SAM surface data. In addition, martian meteorite Chassigny contains trapped noble gases with isotopic ratios similar to solar abundance [11], and has long been considered a pristine, mantle derived sample. However, previous studies of apatite in Chassigny indicate that crustal fluids have interacted with regions interstitial to the cumulus olivine [12-13]. The initial Cl isotope measurements of apatite in Chassigny suggest an addition of crustal component to this lithology, apparently contradicting the rare gas data. Here, we examine the Cl isotopic composition of multiple generations and textures of apatite in Chassigny to extricate the crustal and mantle components in this meteorite and to reveal the style and timing of the addition of crustal components to mantle-derived magmas. These data reveal distinct martian Cl sources whose signatures have their origins linked to both the early Solar System and the evolving martian atmosphere.

Analytical Approach: We identified numerous apatite targets in the Chassigny meteorite using the JEOL electron microprobe housed at the University of New Mexico. The apatite grains were documented through backscatter electron imaging, major and minor elements using X-ray mapping, and quantitative analysis. The apatite ranged in size from 2 to 50

microns. The Cl isotope measurements in this study were carried out by isotopic imaging with the JSC CAMECA NanoSIMS 50L ion microprobe. Isotopic images of ^{16}O , ^{16}OH , ^{31}P , ^{35}Cl and ^{37}Cl were obtained by rastering a 3-4 pA Cs^+ primary ion beam having an impact energy of 16 keV over 8 - 15 micrometer fields of view. Each imaging run consisted of 20 - 40 repeated scans over the same field of view. The spatial resolution of these images was approximately 200 nm. Secondary ions were collected in multi-detection mode using electron multipliers (EMs) at a mass resolving power of $>9,000$, that was sufficient to resolve isobaric interferences. Isotopic images of small apatites included the entire grain, while for the largest grains only a portion of the grain was sampled. Sample charging was mitigated with the use of an electron flood gun. Isotopic images were processed using software developed at JSC by S. Messenger. This software was used to correct for EM deadtime, quasi simultaneous arrival (QSA), and instrumental mass fractionation and to align successive image planes. Images of Snarum apatites were obtained under similar conditions interspersed between sample measurements. Isotopic and elemental ratios were determined from target apatites by defining regions of interest within each image using the ^{31}P image as a reference. This approach allowed ^{37}Cl , ^{35}Cl , and $\delta^{37}\text{Cl}$ to be determined for individual pixels in the rastered

image. Where the $\delta^{37}\text{Cl} = \left(\frac{R_{sa}}{R_{std}} - 1 \right) 1000$, and $R =$

$^{37}\text{Cl}/^{35}\text{Cl}$ ratio of sample (*sa*) and standard (*std*). This approach allowed for the elimination of data in the raster area not resulting from the apatite, the capability to sum data from multiple raster passes to increase precision, and the ability to examine the variation of $\delta^{37}\text{Cl}$ in different portions of the larger apatite (e.g. core versus rim). Precision was less than 1 per mil for the apatites analyzed in Chassigny. An internal standard apatite with a known $\delta^{37}\text{Cl}$ was used to calibrate the analyses. Multiple Cl isotope apatite standards allowed us to examine the effect of Cl concentrations on matrix dependent fractionation. The maximum matrix dependent fractionation was less than 1 per mil for Cl concentrations between 0.20 and 6.5 wt.% Cl. Therefore, for the much more restricted

range in % Cl in the Chassigny apatite, the matrix effect was significantly less.

Results: For this study, we designated three different apatite textural types in the Chassigny meteorite. “Type 1” occurs as anhedral grains closely associated with the intercumulus regions that are interstitial to the olivine. The intercumulus regions of Chassigny consist of 2 feldspars, silica, and glass. These apatites are commonly less than 15 μm . “Type 2” apatite occurs as significantly larger grains (100 μm in length) that are closely associated with the coarse-grained olivine and chromite. Finally, fine-grained apatite (< 5 μm) occurs in large melt inclusions in the olivine. One of the key differences among apatite textural groups is in the composition of their halogen site. Within an OH-F-Cl ternary plot, apatite from Chassigny generally plots along the F-Cl join with some individual grains containing up to 0.1 OH/(OH+Cl+F) component. Type 1 apatite has the highest proportion of Cl in the halogen site with between 0.40 to 0.65 Cl/(OH+F+Cl). The apatites in the melt inclusions have the lowest proportion of Cl in the halogen site with between 0.04 to 0.27 Cl/(OH+F+Cl). Type 2 apatite is intermediate between these two textural types with a Cl/(OH+F+Cl) of 0.35 to 0.40. These ratios translate to a range in Cl from 0.80 to 3.9 wt.% and F from 1.3 to 3.5 wt%. A key observation from the Cl isotopic measurements is that the $\delta^{37}\text{Cl}$ measured in Chassigny apatites exhibit a considerable range ($\approx 10\text{‰}$) that is directly linked to textural type and apatite composition. This range in $\delta^{37}\text{Cl}$ approaches that observed in all martian meteorites ($\approx 15\text{‰}$). The melt inclusion apatites and interiors of the large type 2 apatites are enriched in light Cl, whereas the intercumulate apatites are enriched in heavy Cl.

Discussion: The measurement of the $\delta^{37}\text{Cl}$ in apatite in martian meteorite Chassigny confirms that two Cl isotopic reservoirs exist on Mars: (1) an isotopically light-Cl mantle reservoir ($\delta^{37}\text{Cl} = -4$ to -6‰), which exhibits limited variability and is the same for depleted and enriched mantle sources and (2) an isotopically heavy-Cl crustal reservoir ($\delta^{37}\text{Cl} > 0$), which exhibits significant variability [7-9]. The mantle component is preserved in melt inclusions that also hosts the solar noble gas composition documented in Chassigny [10]. The preservation of these two distinct components in a single meteorite provides petrogenetic insights into the interaction between these two reservoirs and constrains the relationship between two major martian crustal lithologies (chassignites, nakhlites). The existence of these two reservoirs has profound implication for the evolution of the martian atmosphere, the nature of material that accreted to form Mars, and volatiles in the solar nebula. Mars accreted from materials that were dominated by light Cl and probably represent the Cl isotope composition

of the Sun and proto-nebular disk. The enrichment of the crust in heavy Cl resulted from protracted loss of ^{35}Cl to space, started early in the history of Mars. The light Cl signature of accreting materials that formed Mars is different from the Earth, Moon, and many primitive meteorites. These differences represent distinct Cl and volatile reservoirs in the solar nebula. The low $\delta^{37}\text{Cl}$ reservoir represents the primordial Solar System composition from which Mars accreted. The higher $\delta^{37}\text{Cl}$ values observed for the Earth, Moon, and many chondrites are not primordial, rather they represent the later incorporation of ^{37}Cl -enriched HCl-hydrates into accreting material [8].

Swindle [10] used the isotopic composition of Chassigny as the starting point for modeling the mass fractionation of the Martian atmosphere. Examining the potential of crustal and mantle Cl isotope components in Chassigny and the other chassignites will allow us to better unravel the origins of the noble gas components. Finally, the SAM instrument on the Mars Science Lab has reported Cl isotopic composition of material from Gale Crater [9], characterized by a wide variation in $\delta^{37}\text{Cl}$ that is not reproduced in the martian meteorites. Further analyses of $\delta^{37}\text{Cl}$ components in martian meteorites may provide a deeper understanding of these new results from the martian surface.

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